Title: Palladium/Copper Alloy Composite Membranes For High Temperature Hydrogen Separation From Coal-Derived Gas Streams

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Background. For hydrogen from coal gasification to be used economically, processing approaches that produce a high purity gas must be developed. This is particularly true for generation of power in various types of fuel cells. Palladium and its alloys, nickel, platinum and the metals in Groups 3 to 5 of the Periodic Table are all permeable to hydrogen. Hydrogen permeable metal membranes made of palladium and its alloys are the most widely studied due to their high hydrogen permeability, chemical compatibility with many hydrocarbon containing gas streams, and infinite hydrogen selectivity. Our Pd composite membranes have demonstrated stable operation at high temperatures for over 50 days. These membranes consist of a thin (~10 μm) film of metal deposited on the inner surface of a porous metal or ceramic tube. Coal derived synthesis gas may contain up to 15,000 ppm H_2S as well as CO, CO_2, N_2 and other gases. Highly selectivity membranes are necessary to reduce the H_2S concentration to acceptable levels for solid oxide and other fuel cell systems. Pure Pd-membranes are poisoned by sulfur, and suffer from mechanical problems caused by thermal cycling and hydrogen embrittlement. Alloying Pd can suppress the $\alpha \rightarrow \beta$ phase transition caused by hydrogen uptake; therefore, Pd alloys often have greater resistance to thermal cycling. An alloy of Pd containing 40 weight% copper (Cu) has been reported to be substantially more permeable than pure Pd [1-3], more resilient with regard to hydrogen embrittlement [2], and resistant to poisoning by H_2S [1,4]. This abstract summarizes the preparation and fabrication of Pd-Cu alloy composite membranes, and their performance in pure gas transport experiments. Experiments using gas mixtures, including H_2S, are planned in the coming months.

Objective. The feasibility of preparing and using pure Pd-membranes for H_2 separation is well known. Furthermore, the ability of thick Pd-Cu alloy membranes to separate H_2, and the high temperature stability and resistance to poisoning of these materials has been demonstrated. What remains to be shown is that thin (<10 μm) Pd-Cu alloy films that have both high H_2 flux and high selectivity can be fabricated economically. The stability of these films with respect to embrittlement (thermal cycling), sulfur, and other components of coal-derived gas must also be demonstrated.

Experimental. Electroless plating is used to deposit Pd-Cu alloys on tubular porous ceramic supports using a sequential plating method. Sequential plating and subsequent annealing has been used previously to prepare other composite Pd alloy membranes such as Pd-Ag [5] and Pd-Au [6]. An alternative, alloy deposition from mixed plating baths, was shown to be difficult to control [5]. Pd must be deposited first because Cu will dissolve in the Pd plating solution. Pd films are deposited using our improved surface preparation technique using Pd acetate [7] on porous alumina supports using a continuous flow system with an applied osmotic pressure difference [8]. After Pd deposition, the membranes are leak tested at ambient conditions using N_2. Once a defect-free Pd layer has been fabricated, Cu is deposited on top of the Pd layer using electroless plating without an osmotic pressure difference. The electroless Cu bath used is described by Horn [9]. Annealing in H_2 is performed at 350 to 450°C to permit intermetallic diffusion to form a continuous alloy film. Films were characterized by SEM/EDX for thickness and composition.

Results and Discussion. Pure gas transport data for H_2 and N_2 through three composite Pd-Cu membranes are given in the table below. The H_2 flux is continuously measured during the annealing process and the increase to a steady-state flux value is used to demonstrate the formation of a uniform Pd-Cu alloy. Note that the hydrogen flux for the membrane fabricated using an asymmetric 50 nm ultrafilter is much higher than for the membrane supported on a 0.2 µm pore size symmetric support, despite having essentially equivalent Pd alloy film thickness. Electron probe microanalysis is used to measure the composition of the alloy membrane formed and to investigate the uniformity of the film formed during the annealing process, and demonstrates that the Pd and Cu concentration profiles for membrane 9 are very uniform. Membrane #20 was fabricated using a 20 nm pore size ceramic ultrafilter and an **order of magnitude** reduction in membrane thickness was obtained. This observation supports the hypothesis that the metal membrane thickness can be reduced using supports with smaller pore size that have lower surface roughness.

Data summary for Pd–Cu composite membranes, GTC = Coors Ceramics, USF = U. S. Filter. The measured quantities for membranes #20 and #A were obtained at 350 °C are shown by an asterisk.

Membrane #	**Substrate**	**Thickness (µm)**	**Pd Mass (mass %)**	**H_2 Flux @ 450 °C (mole/m^2•s)**	**ΔP (bar)**	**Avg. H_2/N_2 Selectivity @ 450°C**
9	GTC 0.2 µm symmetric	12 - 15	80	0.247	6.90	20.4
10	USF 50 nm ZrO_2 asymmetric	13	90	0.683	3.45	1210
20	USF 20 nm ZrO_2 asymmetric	0.5 - 1	90	0.55*	3.45*	1500*
A	USF 50 nm ZrO_2 asymmetric	0.5 - 1	70	0.60*	3.45*	40*

Accomplishments and Future Plans. Major goals of this project included fabrication of defect free Pd/Cu films and reducing film thickness to the order of 1 μm. These goals have been achieved. In the immediate future film fabrication activities will be directed at obtaining the presumed optimal composition of 40 wt% Cu. Preparation procedures have been modified to produce Membrane A, shown in the Table above, which is 30 wt% Cu. Selectivity for this particular membrane is poor, probably because the 50 nm pore size of the support is too large for an film on the order of 1 μm thick. After optimization of film composition, experiments to tests the resistance of the film to degradation by thermal cycling and poisoning by H_2S will be conducted. Ultimately the Pd/Cu films will be tested using simple gas mixtures of hydrogen, CO and H_2S, and a short term durability test (100 hours) using simulated coal gas containing CO, CO_2, H_2, CH_4, N_2, H_2S, COS, NH_3, and H_2O will be performed on the best membrane.

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List of Journal Articles and Presentations: Grant No. DE-FG2699-FT40585

J. Douglas Way and Robert L. McCormick "Palladium/Copper Alloy Composite Membranes For High Temperature Hydrogen Separation From Coal-Derived Gas Streams" poster presented at University Coal Research Contractors Review Meeting, Pittsburgh, June, 2000.

Robert L. McCormick and J. Douglas Way "Palladium/Copper Alloy Composite Membranes For High Temperature Hydrogen Separation From Coal-Derived Gas Streams" poster presented at ARO Workshop on Fuel Processors for Proton Exchange Membrane Fuel Cells, Detroit, June 19-21, 2000.

J. Douglas Way, Robert L. McCormick, Fernando Roa, and Stephen Paglieri "Palladium-Copper Alloy Composite Membranes for H_2 Separation" invited presentation at the IUPAC Workshop on the Standardization of Methods for the Characterization of Inorganic Membranes, Montpellier, France, June 26, 2000.

J. Douglas Way, Robert L. McCormick, Fernando Roa, "Palladium-Copper Alloy Composite Membranes for H_2 Separation" presented at the Sixth International Conference on Inorganic Membranes, Montpellier, France, June 27-30, 2000.

J. Douglas Way, Robert L. McCormick, Fernando Roa, "New Materials for Gas and Liquid Separations," invited presentation at the Los Alamos National Laboratory, Los Alamos, NM, December 1, 2000.

Fernando Roa, J. Douglas Way, and Robert L. McCormick "Preparation of Micron-Scale, Palladium-Copper Composite Membranes for Hydrogen Separation" presented at the American Chemical Society Spring National Meeting, San Diego, CA, April 4, 2001.

Fernando Roa, J. Douglas Way, and Robert L. McCormick "Palladium-Copper Alloy Composite Membranes for H_2 Separation" invited presentation at North American Catalysis Society Meeting, Toronto, June 3-8, 2001.

Fernando Roa, J. Douglas Way, and Robert L. McCormick "Palladium-Copper Alloy Composite Membranes for H_2 Separation" paper submitted to *The Chemical Engineering Journal* (Elsevier), June, 2001.

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